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Phosphorus sorption, supply potential and availability in soils with contrasting parent material and soil chemical properties.

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Summary

Soil phosphorus (P) management requires a more targeted and soil specific approach than is currently applied for agronomic recommendations and environmental evaluation. Phosphorus buffering capacities control the supply of P in the soil solution and were measured across Irish soils with contrasting parent material and chemical properties. Langmuir sorption buffer capacities (MBC) and binding energies (b) were strongly correlated with soil pH and extractable aluminium (Al). A broken-line regression fitted to the relationship between MBC and Al derived a change-point value for Al above which MBC increased linearly. Soils above the change point were predominantly acidic to neutral with non-calcareous parent material, larger buffering capacities and binding energies than calcareous soils. Ratios of Mehlich3-Al and P (Al:P) were used to relate buffering capacity with supply potential in non-calcareous soils. Large ratios of Al:P were associated with poor P availability, characteristic of strongly P fixing soils. Threshold values of iron-oxide paper strip P (FeO-P) and Morgan's P revealed Al:P ratios where soils began to supply P in available form. The change-point for Morgan's P fell within the current target index for P availability; however, the confidence interval was more compatible with previous agronomic P indices used in Ireland. Relationships between Morgan's P and measures of extractable P, M3-P and Olsen P, deviated in calcareous soils at large soil P contents, indicative of P precipitation processes dominating in these soils. Identifying differences in soil P buffering capacity at laboratory scale would improve agronomic and environmental assessment at field and catchment scales.

Introduction

Phosphorus (P) is an essential element to all known life and an adequate supply is required in agricultural soils to meet the demands for crop growth and grazing animal health. The finite nature of rock phosphate and Europe's dependence on imports from China and Asia and North Africa, is putting its supply under pressure as reserves are diminishing (Cordell *et al.* 2009). The majority (79%) of the P imported is used to make fertilizer for use in agriculture and food production and in animal feeds (11%) (Johnston & Steen, 2000). In many countries, fertilizer P recommendations are based on P index systems where bands of soil test P values are used to guide application rates. In Ireland the agronomic soil test for P is Morgan's extractable P, and for easier management and knowledge transfer at the farm scale Morgan's P levels have been categorized as indices; 1 (deficient), 2 (low), and 3 (agronomic optimum) and 4 (excessive) (Lalor & Coulter, 2008). Fertilizer recommendations have been inextricably linked with soil tests since the 1950s and 1960s, following the general philosophy of 'build up and maintenance' (Vos, 1998). In recent years the agri-environmental landscape has changed, especially, since the implementation of water quality directives.

. Morgan's P values are now used as the basis for risk assessment of P loss from Irish soils. Going forward, farmers face huge challenges in managing P resources on farms including increased P requirements for sustainable intensification to meet rising global food demands, the maintenance of soil fertility under stringent environmental constraints and increasingly expensive P fertiliser. The growing need for economic and environmental sustainability has stimulated interest in efficient P fertilizer utilization and nutrient management on farms.

Future soil fertility management requires a more targeted and soil specific approach than is currently applied, to maximize the crop use efficiency of valuable P inputs, and to increase the P supplying capacities of soils under reduced P input regimes. Phosphorus

buffering capacity is described as the ability to supply soluble P as a function of capacity, and differences in P buffering and sorption capacities can significantly influence supply and availability of P in a water soluble form (Burkitt *et al.* 2001).

Whilst it has been accepted that no soil test is universal (Vos, 1998), recent research incorporating P sorption and buffering with soil P tests, has provided P indices that are soil-type specific for improved critical soil test P predictions to give a value of soil test P where availability is optimized (Moody *et al.* 1997; Van Rotterdam *et al.* 2010). Similarly, quality/intensity relationships have provided useful indices for predicting supply of slowly available P in soils using easily measured soil properties with traditional soil tests (McLaren *et al.* 2014; Van Rotterdam *et al.* 2012). More recently, Reijneveld *et al.* (2014) proposed a strategy for modelling novel methods of P capacity and intensity, with historical P tests, combined with field trials, for agronomic recommendations and environmental evaluations.

Over the past decade Irish fertiliser P recommendations have been updated for grassland soils in Ireland, using results from a fertilizer response trial that did not differentiate soil type, (Schulte & Herlihy, 2007). The objectives of this present study were to measure P buffering capacities across a range of Irish grassland soils with contrasting parent material and chemical properties and relate these values to soil attributes, pertaining to P availability and supply. Soil samples with contrasting parent material and chemistry were collected from grassland sites across Ireland and the relevance of contrasting soil P buffering and sorption is discussed with regard to availability and examined in the context of our current revised agronomic recommendations.

Materials and methods

Soil Sampling

Principal agricultural soils were identified from the General Soil Map of Ireland (Gardiner & Radford, 1980), the mapping unit of which is the soil association. These include amalgamations of Great Soil Groups and associated parent material, and for this study, 120 sampling locations were identified that best represented principal soil associations used in grassland systems in Ireland (Table 1). The soil sampling programme also targeted sites with a range of soil test P levels (Morgan's P) so that the agronomic P indices were reflected in the data. Samples were taken on field-by-field basis to a depth of 100 mm with a soil corer (1.5-cm diameter) with approximately 30–40 cores bulked to provide a composite sample from each field and prior to the spreading of fertilizers and manures. One hundred and twenty samples were air-dried and sieved to remove roots and stones (2 mm mesh) and stored in air-tight boxes at room temperature prior to analysis.

Phosphorus sorption isotherms

Phosphorus sorption isotherms were derived using a modification of the standardized batch technique by Nair *et al.* (1984). Because of the time consuming nature of this technique, a sub-set of 74 soil samples, representing each soil association, were equilibrated with P in solution and the data was evaluated using the Langmuir model (Paulter & Sims, 2000) as follows. Six, 40-ml solutions of P concentration 0, 5, 10, 15, 20 and 25 mg l⁻¹ in KH₂PO₄ were added to 2 g soil samples in 50ml centrifuge tubes in duplicate. The suspensions were shaken at room temperature for 24 hour, centrifuged and filtered, and the concentration of P in solution was measured colorimetrically (John, 1970) using the molybdate blue method. Phosphorus sorbed to the soil was calculated as the difference between initial concentration

and P concentration measured at equilibrium. Adsorption data and affinity constants were determined by fitting sorption data to the Langmuir isotherm equation:

$$C/X = 1/X_m \times b + C/X_m, \quad (1)$$

which represents a straight line where X is P sorbed (mg P kg⁻¹), C is the equilibrium P concentration (mg P l⁻¹) with an intercept 1/X_m x b and slope 1/X_m. The linear form of the Langmuir equation was then used to derive X_m, the sorption maximum (mg P kg⁻¹) and b, a constant related to the binding energy (l mg⁻¹). Phosphorus sorption isotherms were plotted for each soil sample collected and the Langmuir model derived sorption maximum (X_m, mg kg⁻¹), binding energy (b, l mg⁻¹). Maximum buffer capacity (MBC, l kg⁻¹) was calculated as the product of X_m and b (Indiati *et al.* 1999).

Extractable P (FeO-P, Olsen P, Mehlich3-P, Morgan's P)

The iron-oxide paper strip test was used as a P sink method for estimating labile inorganic P on 120 soils sampled, according to the method of Menon *et al.* (1988). One FeO-impregnated paper strip (100 x 20 mm) was added to each sample of soil (1 g) suspended in 40 ml of 0.01 M CaCl₂ solution and shaken for 16 hour on an end-over-end shaker. The paper strips were eluted with 40 ml 0.1 M H₂SO₄ for one hour and the P concentrations in the acidic solution determined colorimetrically. Morgan's P was determined on 120 soils, with 6.5 ml of soil in a buffered acetate-acetic acid reagent at a 1:5 (v/v) soil to solution ratio extracting for 30 minutes (Peech & English, 1944). Mehlich3-P (M3-P) was determined on 120 soils using the modified Mehlich test (Mehlich, 1984) to extract P, aluminium (Al), iron (Fe) and calcium (Ca), at a 1:10 soil solution ratio of 2 g of soil shaken with 20 ml Mehlich3 reagent (0.2 M CH₃COOH + 0.25 M NH₄NO₃ + 0.015 M NH₄F + 0.13M HNO₃ + 0.001M EDTA) for 5 minutes on a reciprocating shaker. The extracts were filtered and P in solution measured colorimetrically with a molybdate blue method (John, 1970). Olsen P was measured on 60

samples only because of a lack of sample availability. This method used 2-g sample shaken with 40 ml 0.5 M NaHCO₃, buffered at pH 8.5, for 30 minutes. Phosphorus concentration in the solution was determined colorimetrically with a molybdate blue method (John, 1970).

Soil pH was determined on a 2:1 soil-water ratio paste on 120 samples and percentage organic matter (% OM) measured from 120 samples as the loss-on-ignition of 5-g samples at 500° C. Results were analysed with SAS Enterprise Guide V5 to obtain correlation and regression information. The NLMIXED procedure in SAS was used for change-point analysis and broken-line regression. Optimization was performed using the dual quasi-Newton algorithm, with a dual Broyden, Fletcher, Goldfarb, and Shanno (BFGS) update of the Cholesky factor of an approximate Hessian. PROC NLMIXED computes approximate standard errors for estimates and predictions using the delta method of truncated expansions.

Results

Chemical properties of soils collected

Soil chemical properties of representative soil associations are presented in Table 2 and their correlations are tabulated in Table 3. Soil pH ranged from 4.7–7.1, with smallest values measured in soil associations 14, 15 and 25 and largest values recorded in soil associations 30 and 34 on limestone parent material. Extractable Ca, ranged from 284-8660 mg kg⁻¹ across all soils and was positively correlated with soil pH ($r = 0.80$). Extractable Al and Fe ranged from 69-1730 mg kg⁻¹ and 215-666 mg kg⁻¹, respectively with largest concentrations measured on soil associations 14 and 25. Extractable Al was negatively correlated with soil pH ($r = -0.71$) and largest concentrations associated with acidic soils. Across all soil associations, OM% ranged from 5.3–15.7 % and some weak but significant correlations were observed between OM% and extractable Fe ($r = 0.47$) and Ca ($r = 0.32$) possibly indicating

the presence of amorphous forms of Fe and Ca among these soils. Morgan's P ranged from 1.5–32.9 mg l⁻¹ and correlated with other P extraction methods, where the strongest correlations were observed with M3-P ($r = 0.79$) and FeO-P ($r = 0.73$) and weakest with Olsen-P ($r = 0.63$). Across all soils, Mehlich3 extracted of the most P (13.4–285 mg kg⁻¹), followed by FeO-P (15.4–128 mg kg⁻¹) and Olsen-P (8.9–89.6 mg kg⁻¹).

Langmuir sorption properties

The Langmuir model provided a highly significant ($P < 0.001$) fit to soils in this study ($R^2 > 0.95$) and values of Langmuir parameters X_m , b and MBC derived from the isotherms across all soil associations are presented in Table 2. Soil pH was inversely correlated with all of the Langmuir sorption parameters X_m , ($r = -0.46$), b ($r = -0.62$) and MBC ($r = -0.65$) whilst extractable Al positively correlated with X_m , b and MBC. These soil attributes provided the strongest correlations with Langmuir sorption terms, although the scatter plots were nonlinear. Soil pH accounted for 55% of the variation in log transformed MBC (Figure 1) with buffering capacity decreasing as soil pH increased from 4.7 to 7.1. The regression equation is listed in Table 4. Soil associations derived from limestone parent material recorded the smallest values of each of the Langmuir terms with typically high pH values of >6.0 . Visual inspection of the relationship between MBC and Al indicated small MBC values at small Al values with a sharp increase in MBC above a threshold Al value. This threshold value was derived by regression modelling of the data where a broken-line regression was fitted to log transformed MBC and extractable Al in Figure 2, and a significant change-point ($P < 0.001$) derived at an Al concentration of 612 (± 104) mg kg⁻¹, above which buffer capacity in soil increased linearly with increasing Al. Parameter estimates for this relationship are presented in Table 5. Above the upper confidence limit of the change-point for Al (>716 mg kg⁻¹), soils was predominantly derived from non-calcareous

parent material. This group of soils were characterised by predominantly low pH values ranging from 4.7 to 6.3 (mean = 5.3) and strong Langmuir sorption properties. Mean MBC and b values in these soils were 1250 l kg⁻¹ and 2.56 l mg⁻¹, respectively, and mean Al and Ca values of 1072 and 1451 mg kg⁻¹, respectively. These soils are denoted here as non-calcareous soils (n = 76) and their summary statistics are presented in Table 6. When separated out from the overall data, Al in these soils accounted for 65% and 57% of the variation in MBC and b, respectively. The remaining soils, were mostly soil associations derived from limestone parent material, with soil pH in the range 5.2–7.1, mean extractable Ca values of 3487 mg kg⁻¹, and mean MBC and b values of 346 l kg⁻¹ and 1.01 l mg⁻¹, respectively. These soils are denoted here as calcareous (n = 44). There were no significant correlations between Al, Ca and Fe and any of the Langmuir sorption values in the calcareous soils group. Four samples with Al values of (776–779 mg kg⁻¹) that exceeded the upper value of the 95% confidence interval around the change-point were assigned to the calcareous group because of parent material, large Ca values and weak Langmuir sorption properties.

Aluminium to phosphorus ratios in non-calcareous soils.

There was no direct correlation between the Langmuir terms and the different measures of extractable P, except for a weak correlation between X_m and FeO-P ($r = 0.26$). Given that buffering capacity and affinity in non-calcareous soils was strongly associated with extractable Al, the ratio of M3-Al and M3-P (Al:P) was used to infer sorptive capacity and ability to supply P, in these soils. This ratio describes capacity and affinity for P, relative to P already sorbed. The weight ratios developed for Al:P were in line with other studies using Ca:P ratios (McLaren *et al.* 2014) with practical significance since soil testing laboratories tend to record results on a weight basis. To relate P buffering to supply in soluble and plant available forms, ratios of Al:P were plotted against P desorption and availability as measured

by FeO-P and Morgan's P and the relationship is depicted in Figures 3(a). The smallest FeO-P values corresponded to large Al:P ratios, however, as Al:P ratios decreased towards a point of inflection on the graph, below which, FeO-P increased steadily. Following the pattern in the data, a broken line regression was fitted and a significant change-point was found ($P < 0.001$) at the FeO-P value of 43.2 mg kg^{-1} within a lower and upper 95% confidence interval of 32.3 and 53.9 mg kg^{-1} , respectively. The value of Al:P at this change-point was 8.1 within a confidence interval of 5.5 and 11.8, respectively. To relate buffering to agronomic P, the relationship between Al:P and Morgan's P was examined and a significant change-point was found in the relationship ($P < 0.001$). A broken line regression fitted to the data derived a change-point for Morgan's P at 7.3 mg l^{-1} within a 95% confidence interval of 5.9 and 8.7 mg l^{-1} (Figure 3(b)). The value of Al:P at the Morgan's P change-point was 11.7 within the confidence interval of 9.2 and 15.0. Since the estimate of 11.7 for Al:P at the Morgan's P change-point falls within the confidence interval for value of Al:P at the FeO-P change-point, they are not significantly different. Thus the Al:P ratio at the Morgan's P change-point is consistent, within the range of possible values estimated at the FeO-P change-point. The parameter estimates for relationships in Figure 3(a) and 3(b) are presented in Table 5.

Calcium to P ratios in calcareous soils

Mehlich3 extractable Ca and P were expressed as a ratio (Ca:P) and plotted against values of FeO-P and Morgan's P in a similar analysis for calcareous soils. One sample with an extremely large Ca value of 8888 mg kg^{-1} which biased the relationship was removed from the analysis and a non-linear, negative relationship between Ca:P and FeO-P ($R^2 = 0.32$) and Morgan's P ($R^2 = 0.33$), was observed. These relationships showed no change points above or below which, P became more or less available, and the regressions were not strong enough to be predictive.

246

247 *Relationship between P tests in calcareous and non-calcareous soils.*

248 The standard agronomic P test used in Ireland, Morgan's P, was significantly correlated with
249 each of the other extractable P methods FeO-P ($r = 0.73$), M3-P ($r = 0.79$) and Olsen-P ($r =$
250 0.63) across all soils. Correlations across all soils may conceal the effect that variations in Al
251 and Ca could have on extraction efficiency in the soils presented in this study. Figures 4(a)
252 and 4(b) depict the relationship between Morgan's P and measures of available P M3-P,
253 Olsen-P, for non-calcareous and calcareous soil groups. The relationships between Morgan's
254 P and M3-P, and Olsen P were broadly similar within each of the soil group, however, they
255 deviated as soil P concentrations increased, indicating less extractable M3-P and Olsen-P at a
256 given Morgan's P concentration in the calcareous soils. The relationship between FeO-P and
257 Morgan's P (Figure 5) was more comparable between soil groups within the typical
258 agronomic range (Morgan's P 0–10 mg l⁻¹) but had some divergence in the relationship at
259 very large P values. However, only a small number of samples were present at extremely
260 large Morgan's P values. Overall, the relationships between these variables was stronger in
261 non-calcareous ($R^2 = 0.71$) compared to calcareous soils ($R^2 = 0.42$) and the regression
262 equations between soil tests are presented in Table 4.

263

264 **Discussion**

265

266 *Langmuir sorption properties and soil characteristics*

267 Values of Langmuir sorption parameters in this present study are in line with those reported
268 elsewhere on agricultural soils over a soil pH range 4.6–8.3 (Indiati *et al.* 1999). These
269 authors reported X_m ranging from 37.2–4990 mg kg⁻¹, b values from 0.75–6.12 l mg⁻¹ and
270 MBC values from 51.4–5260.8 l kg⁻¹. Quintero *et al.* (1999) reported a decrease in P

retention and maximum buffering capacities in soils as pH increased from 3 to 7, and attributed a strong buffering capacity to large amounts of both Al and Fe, in line with results reported here. Calcareous soils in this present study recorded small values of X_m , b and MBC and which are in line with those reported by Amrani *et al.* (1999) on calcareous soils in Manitoba with Langmuir buffer capacities and affinity values between 146 – 808 l kg⁻¹ and 0.15 - 0.6 l mg⁻¹, respectively.

Soils grouped as non-calcareous exhibited greater X_m , b and MBC, because of their greater amounts of extractable Al. Broggi *et al.* (2011) found significant influence of soil pH and Al content, with smaller adsorption energies in limed soils. In this present study, soil pH and Al were negatively correlated with each other and associated with strong P sorbing soils. The strong association between P sorption and amounts of extractable Al in preference to Fe is also in line with other international, (Burkitt *et al.* 2002; Paulter and Sims, 2000) and Irish studies (Daly *et al.* 2001; Maguire *et al.* 2001). Consistent with results reported here, some researchers reported Al to be more strongly correlated than Fe with P sorption (Villapando & Graetz, 2001). Extractable Al is also strongly associated with plant growth and Ballard & Fiskell (1974) concluded that the dominant nature of extractable Al provides the best indicator of P retention in soils.

Relating sorptive properties to P supply

To relate measures of extractable P to sorptive properties, the relationship between ratios of M3 extractable Al:P and FeO-P was described by a broken-line regression with change-points which revealed a value for Al:P below which FeO-P concentrations increased steadily. Above this Al:P change-point, soils were characterized as strongly P sorbing, indicative of poor Al-P solubility. A similar relationship was found between Al:P and Morgan's P and the change point corresponded to a Morgan's P value of 7.3 mg l⁻¹. This value falls within the

upper end of the current soil test P index range for optimum P availability (5.1–8 mg l⁻¹) set for Irish soils by Schulte & Herlihy (2007). Above the Al:P change-points for both FeO-P and Morgan's P it is likely that the P sorbed on surface oxides of Al was more tightly sorbed and less available for release as soluble and plant available forms. Once the amounts of P increased in the soils and reduced the Al:P ratios below the change point values, the soils began to supply P in soluble and plant-available forms. The Al:P values at the change-points for both FeO-P and Morgan's P were consistent and not statistically different. Soils below the change-point were typified by large MBC and b values, with low pH and large Al concentrations and are described here as strong 'P fixing' non-calcareous soils. Quintero *et al.* (1999) reported that 70 % of added P in strongly P fixing soils remained in the non-labile P pools, whereas 30–40 % of P added to soils with poor buffering capacity was non-labile, and noted that greater rates of fertilizer P are required for soils with large Al and Fe contents to reach an optimum P availability for plant uptake. Similarly, Fernandez & Warren (1994) related different sorption properties to varying amounts of extractable Al and concluded that fertiliser rates should vary according to amount of Al in soils. Our results implications for fertilizer recommendations on strong P fixing soils where Al:P ratios are large although require further data to be able to revise existing recommendations. However, this work provides easily measured soil properties (Al:P) that can be combined with conventional soil testing to describe P supply potential across soils with different sorptive properties.

Interpreting the Morgan's P threshold within agronomic P indices.

Across the soils studied here the change-point value for Morgan's P of 7.3 mg l⁻¹ in Figure 3(b) represents the ability to supply P in a plant available form consistently. Accounting for some of the variability between soils a confidence interval around this change-point Morgan's P concentration of 5.9 to 8.7 mg l⁻¹ was calculated. This range is possibly more

compatible with the previous target index (Index 3) range of 6.1 to 10 mg l⁻¹ Morgan's P (Coulter, 2004), before they were revised downward to 5.1–8 mg l⁻¹. These revised values were based on grass yield response studies of a range of fertilizer P inputs over 8 soil series (Schulte & Herlihy, 2007). However, the soils used in the latter trial comprised of four limestone and four non-limestone parent material soil groups, and did not cover the range of soil chemistry found in soils in Ireland. The fertilizer rates required to reach 95% potential yield and herbage P concentration of 3.0 g kg⁻¹ were not statistically related to differences between soil types or parent material groups. The lack of contrast in soil chemical properties across the eight soil series failed to provide the statistical significance required to include soil type as a factor and ultimately resulted in a P index system that does not account for differences in P sorption or buffering capacities that could influence fertilizer uptake and critical soil P values.

The difference in P sorption characteristics between calcareous and non-calcareous soils in this present study results largely from contrasting soil properties such as soil pH and extractable Al and Ca. Herlihy & McGrath (2007) found no significant difference in Langmuir sorption maxima among soil series and soil parent material groups (limestone verses non-limestone) with the exception of equilibrium buffer capacity (EBC) values for the range 0-3 mg l⁻¹ P where there were larger values were observed in the non-limestone soil groups. They also reported no significant differences in pH, clay, oxalate-extractable Al, with the exception of significantly larger oxalate extractable Fe in non-limestone soils. The lack of contrast between their soil groups in terms of chemical properties made it difficult to statistically distinguish sorption characteristics in their data.

Processes of sorption and precipitation: implications for soil P management

In line with previous studies on Irish soils, extractable inorganic P as measured by M3-P, Olsen-P and FeO-P were strongly correlated with Morgan's P on soils collected in this study (Daly *et al.* 2001; Daly & Casey, 2005; Herlihy *et al.* 2006). However, the contrast in soils, exhibited by differences in Langmuir sorption properties, soil pH and amounts of extractable Al, Fe and Ca, influenced the relationships between extractable P and Morgan's P. These relationships indicated larger Olsen and M3-P concentrations in non-calcareous soils and smaller concentrations in calcareous soils, at similar Morgan's P values, particularly as soil test P concentrations increased. The relationship between Olsen-P and Morgan's P was reported for 199 soils sampled in the cross-border region of Northern Ireland (Foy *et al.* 1997) and although the soil tests were strongly related ($R^2=0.70$), the authors reported the Olsen-Morgan relationship in high pH soils and soils over carboniferous geology followed a different trend in predicting the smallest Olsen-P values. The relationship between Morgan's P and Olsen-P in this present study concurs with Foy *et al.* (1997) with the smallest Olsen-P values observed in the calcareous soils at similar Morgan's P values. Morgan's P may be over-estimating Olsen-P and M3-P at large P values P in calcareous soils, where the process of Ca-P precipitation becomes dominant at large soil P contents.

The FeO-P values were more comparable in non-calcareous and calcareous soil groups at similar Morgan's P value and the relationship showed only slight divergence at greater extremes of soil test P concentrations. The FeO-P test is reported to be a 'P sink' method, favoured over chemical extraction for estimates of P desorption and for quantity intensity relationships, as it is not confounded by chemistry (McLaren *et al.* 2014; Van Rotterdam *et al.* 2012) and suitable across soil types.

These diverging relationships indicate stronger sorptive properties in highly buffered soils (Dougherty *et al.* 2011) with a larger pool of P in non-calcareous soils that can continuously supply P to the soil solution and precipitation of Ca-P at large P values in

calcareous soils. Chemical fractionation on calcareous soils has recorded 98% of total inorganic P as Ca-P and desorption from the soil matrix using FeO strips was related to labile P available for plant uptake (Ahmad *et al.* 2006). The interaction of P with soil components in calcareous soils is controlled by both surface reactions and precipitation and at small P concentrations non-carbonate clays provide surfaces for P adsorption. However, once these sites have been filled, and at greater soil P concentrations, calcium carbonate plays a role in the precipitation of P and subsequent reduction of P availability to the plant and soil solution (Von Wandruszka, 2006).

Precipitation of Ca-P in soils at large P values could have implications for P transport at the catchment scale. Mellander *et al.* (2012) recorded sub-hourly P concentrations and discharge delivered to spring water in a karst catchment in western Ireland characterized by calcareous parent material overlain by shallow soils. Despite a large proportion of soils measuring excessive Morgan's P concentrations with a good connectivity to groundwater, background P concentrations in groundwater were small and posed a low risk of increasing surface water P concentrations. The authors conclude that processes of P attenuation in the soil, geology and hydrology in this catchment were limiting P transfers to surface waters. Smaller values of M3-P at large Morgan's P values in the calcareous soils in our study supports the attenuation hypothesis in Mellander *et al.* (2012) that the process of desorption is overtaken by precipitation at elevated soil P contents.

Herlihy *et al.* (2004) reported results from a P trial that included a 'zero P treatment' on soils across the full range of soil P indices (1–4) used in Ireland, for both calcareous and non-calacareous soil parent material groups. They reported more rapid rates of decline in soil test P in limestone soils at low P indices that could possibly be explained by the poorer buffering in these soils compared to the non-limestone soil group. As P is depleted from the soil solution phase from plant uptake and not replaced in added fertilizer, soils that are better

buffered can utilise their larger store of labile inorganic P reserves to replenish the soil solution phase more rapidly than poorly buffered soils with smaller overall P reserves which may be more tightly held in the shorter term. Strongly buffered soil will exhibit a slower rate of decline in soil test P concentration than poorly buffered soils over time and modelling studies on Irish soils (Schulte *et al.* 2010) could consider including sorptive properties such as Al:P to improve estimates.

Differences in soil P supply and release between calcareous and non-calcareous soils have implications for how P fertilizer application should be managed. For non-calcareous soils splitting the annual P allowance using a little and often approach to P application for grassland, over the annual growing season may be more appropriate for maintaining adequate P in soil solution for soils with P concentrations below the change-point for Morgan's P ($< 7.3 \text{ mg l}^{-1}$) with Al:P ratios above those at the change-point. Above the threshold Morgan's P value, maintenance P applications could be applied at the start of the growing season. In contrast it may be less important to split the annual P application for calcareous soils as a smaller proportion of added P would be fixed. In terms of P build-up, calcareous soils may require less P fertilizer overall than strong high P fixing soils to build up to the agronomic optimal range (Index 3) because the binding energies are less in these soils.

Conclusions and Recommendations

Phosphorus dynamics in grassland soils are controlled by the chemical nature of the soil and the P retained in soil. In this study, P sorptive capacity and strength to which P is bound in soil was to a large extent influenced by soil pH and amounts of extractable Al. This was illustrated by a change-point value of extractable Al in soil, above which P buffering capacities increased linearly, facilitating the classification of soils into calcareous and non-

calcareous groups. Non-calcareous soils with large buffering capacities had larger P reserves at similar soil test P than calcareous soils with smaller P buffer capacities. Acknowledging differences in P buffering capacities in grassland soils, combined with soil P testing, could improve P management and efficiency; however, sorption isotherms are too time consuming for routine soil testing. Ratios of Al:P could be used as a surrogate for Langmuir buffer capacities in non-calcareous soils, as this indicator was related to supply potential and release of P in an available form. This indicates the potential for incorporating easily measured soil chemical properties with agronomic P testing, particularly for strong P fixing soils where P availability could be improved by adjusting Al:P ratios. Diverging relationships between soil P tests in calcareous and non-calcareous soils can be attributed to differences in P reserves in strongly buffered non-calcareous soils, and P precipitation at large P contents, in calcareous soils with poor P buffering capacities. Distinguishing differences in P buffering in soil, at process scale, will support improved agronomic and environmental assessment at both field and catchment scale, specifically, our interpretation of P build up and release, P balances, rates of soil P decline and P attenuation in catchments.

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Table 1 The locations and description of soil associations used for sample collection, describing arrangements of Great Soil Groups and associated parent material with texture and drainage class included (Gardiner & Radford, 1980).

Location	Soil Association	Great Soil Groups	Parent Material	Texture class	Drainage class
Tipperary	34	Luvisol (70%), Gleysol (20%), Cambisol (10%)	Gravelly limestone till	Gravelly loam	Well drained
Tipperary	30	Luvisol (70%), Cambisol (20%), Gleysol (5%), Histosol (5%).	Calcareous, limestone till	Sandy loam	Well drained
Cork	15	Podzol (60%), Cambisol (20%), Gleysol (20%)	Old red sandstone, shale	Gravelly loam	Well drained
Roscommon	31	Luvisol (80%), Gleysol (10%), Cambisol (5%), Histosol (5%).	Calcareous glacial till	Loam	Well drained
Tyrone	25	Gleysol (50%), Cambisol (40%), Histosol (10%)	Silurian sandstone-shale composition	Clay loam	Imperfect to poor
Meath	14	Cambisol (75%), Gleysol (15%), Podzol (10%)	Ordovician shale, glacial till.	Loam	Well drained

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Table 2. Range (min-max) of soil properties measured across samples collected from soil association listed in Table 1. Soil pH, %Organic matter (% OM), Morgan’s P, Iron-oxide paper-strip P (FeO-P), Mehlich3 extractable Al, Fe, Ca and P (M3-P) were measured on all soils (n = 120). Across soil associations Langmuir sorption isotherm values were derived for a subset of samples (n = 74). Olsen extractable P (Olsen-P) derived for a sub-set of soils (n = 60) did not include soil associations 30 and 14.

Soil Associatio n	pH	OM	Al	Fe	Ca	Xm	Langmuir Terms		Morgan’s P	Phosphorus Extracts		
							b	MBC		M3-P	FeO-P	Olsen-P
							/ l mg ⁻¹	/ l kg ⁻¹		/ mg l ⁻¹	/ mg kg ⁻¹	
34	5.2-7.0	5.7-15.4	69-1160	215-642	1420-8660	263-333	0.66-4.48	213-476	1.5-32.9	18-168	21.6-38	14.6-57.6
30	5.4-7.1	5.5-11.9	349-780	254-592	1795-5543	263-400	0.63-1.29	250-417	1.6-17.5	17.8-101	19.6-69.6	
15	5.0-6.7	8.3-15.7	580-1530	454-655	894-5674	270-625	0.54-2.71	147-1429	6.6-18.2	60.8-211	39.8-83.2	30.6-77.5
31	4.9-6.9	5.9-15.5	317-1240	306-612	777-5040	303-435	0.35-2.0	119-769	1.5-11.8	13.4-110	15.4-58.4	8.9-34.2
25	4.8-6.3	5.3-14.5	901-1730	390-666	284-3566	385-588	1.43-7.67	714-3333	1.8-25.8	18.4-285	15.4-128	15.5-89.6
14	4.7-6.4	7.5-14.7	254-1730	373-556	769-4721	357-556	1.0-2.89	435-1429	2.6-9.2	30.5-114	17.4-59.2	

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578 **Table 3.** Pearson product moment correlation matrix of r-values significant at $P = 0.05$ derived between soil pH, % organic matter (OM),
 579 Mehlich3 extractable P, Al, Fe and Ca / mg kg⁻¹, Morgan's P / mg l⁻¹, Olsen-P / mg kg⁻¹ and iron-oxide paper strip P (FeO-P / mg kg⁻¹). Sorption
 580 properties include Langmuir sorption maximum (Xm / mg kg⁻¹); binding energy, (b / l mg⁻¹) and maximum buffer capacity, (MBC / l kg⁻¹). NS
 581 denotes non-significant correlation at $P = 0.05$.

	Xm	B	MBC	Morgan's P	M3-P	FeO-P	Olsen-P	pH	OM	Al	Fe	Ca
Xm	1.00											
b	0.38	1.00										
MBC	0.53	0.98	1.00									
Morgan's P	NS	NS	NS	1.00								
M3-P	0.41	NS	NS	0.79	1.00							
FeO-P	0.26	NS	NS	0.73	0.78	1.00						
Olsen-P	NS	NS	NS	0.63	0.88	0.78	1.00					
pH	-0.46	-0.62	-0.65	0.23	NS	NS	NS	1.00				
OM	0.29	NS	NS	0.31	0.37	0.23	0.42	NS	1.00			
Al	0.53	0.76	0.80	NS	0.22	NS	NS	-0.71	NS	1.00		
Fe	0.48	0.41	0.48	NS	0.40	NS	0.43	-0.48	0.47	0.55	1.00	
Ca	NS	-0.57	-0.58	0.24	NS	NS	NS	0.80	0.32	-0.66	-0.40	1.00

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Table 4 Regression equations for relationships between logMBC and soil pH across all soils, and relationships between Morgan's P and extractable measures of soil P, namely, Mehlich3-P, Olsen-P and iron-oxide paper strip P (FeO-P) for both calcareous and non-calcareous soils.

y	Equation		Coefficients	Standard errors	R^2
logMBC	$y = a + (b \times \text{pH})$	a	4.92	0.23	0.55
		b	-0.37	0.04	
M3-P non-calcareous soils	$y = a + (b \times \text{Morgan's P})$	a	8.14	5.59	0.83
		b	11.01	0.58	
M3-P calcareous soil	$y = a + (b \times \text{Morgan's P})$	a	22.47	4.35	0.80
		b	4.67	0.38	
Olsen-P non-calcareous soils	$y = a + (b \times \text{Morgan's P})$	a	9.34	3.82	0.66
		b	3.52	0.38	
Olsen-P calcareous soils	$y = a + (b \times \text{Morgan's P})$	a	15.64	4.19	0.62
		b	1.18	0.27	
FeO-P non-calcareous soils	$y = a + (b \times \text{Morgan's P})$	a	5.18	2.59	0.71
		b	3.68	0.27	
FeO-P calcareous soils	$y = a + (b \times \text{Morgan's P})$	a	21.68	3.00	0.42
		b	1.39	0.26	

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Table 5 Parameter estimates derived from the broken-line regressions fitted to non-calcareous soil data with change-points ($x = c$) highlighted in bold, for extractable Al mg kg⁻¹, FeO-P mg kg⁻¹ and Morgan's P mg l⁻¹.

		Estimate	Standard error	t value	<i>P</i>	95% confidence limit	
						Lower	Upper
Figure 2 (n = 73)	Intercept 1	6.1799	0.3299	18.73	<0.0001	5.5217	6.8381
	Slope 1	-0.0008	0.0007	-1.22	0.2280	-0.0023	0.0005
	x = c	611.92	52.1751	11.76	<0.0001	507.83	716.01
	Value of logMBC at change-point	5.6331	0.1324	42.54	<0.0001	5.3690	5.8973
	Slope 2	0.0029	0.0002	13.08	<0.0001	0.0024	0.0033
Figure 3(a) (n = 76)	Intercept 1	3.9422	0.1433	27.51	<0.0001	3.6568	4.2276
	Slope 1	-0.0402	0.0054	-7.40	<0.0001	-0.0511	-0.0294
	x = c	43.1187	5.4313	7.94	<0.0001	32.3013	53.9361
	Value of logAl:P at change-point	2.2048	0.1692	13.03	<0.0001	1.8678	2.5417
	Slope 2	-0.00861	0.004052	-2.12	0.0369	-0.1668	-0.0005
Figure 3(b) (n = 76)	Intercept 1	4.2247	0.1627	25.92	<0.0001	3.9006	4.5487
	Slope 1	-0.2297	0.0311	-7.37	<0.0001	-0.2917	-0.1676
	x = c	7.3041	0.7153	10.21	<0.0001	5.8794	8.7287
	Value of logAl:P at change-point	2.5471	0.1148	22.19	<0.0001	2.3185	2.7756
	Slope 2	-0.06198	0.01129	-5.49	<0.0001	-0.0844	-0.0395

Table 6 Summary statistics of general soil properties; pH, % organic matter (OM), Mehlich3 extractable Al, Fe, Ca, P, Morgan's P and iron-oxide paper strip P (FeO-P) of soils divided into non-calcareous (n = 76) and calcareous (n = 44) soil groups. Langmuir sorption isotherm data, sorption maxima (Xm), maximum buffer capacity (MBC), binding energy (b) in non-calcareous soils (n = 41) and calcareous soils (n = 33). Olsen-P values were measured on a subset of non-calcareous (n = 47) and calcareous soils (n = 14).

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	Soil pH	OM /%	Al	Fe	Ca	Langmuir Terms			Phosphorus Extracts			
						Xm	b	MBC	Morgan's P	M3-P	FeO-P	Olsen- P
						/mg kg ⁻¹			/mg l ⁻¹	/l kg ⁻¹	/mg l ⁻¹	/mg kg ⁻¹
Non-calcareous soils												
Min	4.7	5.3	807	369	284	303	0.80	244	1.5	13.4	3.3	8.9
Max	6.3	18.3	1730	666	4713	625	8.00	3333	25.8	285	128	89.6
Median	5.2	9.5	1072	553	1451	476	2.56	1250	7.0	85.9	30.4	37.3
Mean	5.3	10.1	1108	540	1631	467	3.04	1417	8.15	98	35.6	40
Calcareous soils												
Min	5.2	5.5	68.9	215	777	244	0.35	119	1.5	17.8	4.4	16.8
Max	7.1	16.3	794	642	8660	667	2.10	1000	32.9	168	69.6	57.6
Median	6.2	9.3	658	425	3539	323	0.94	303	7.1	56.1	31	27
Mean	6.2	9.9	597	432	3457	343	1.01	346	9.0	64.7	34.3	31

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Captions for figures

Figure 1. The relationship between log transformed Langmuir maximum buffer capacity (MBC) and soil pH ($R^2 = 0.55$) for the sub-set of samples for which sorption isotherms were derived (n= 74).

Figure 2. Broken-line regression fitted to the relationship between log transformed Langmuir maximum buffer capacity and extractable for the subset of samples for which sorption isotherms were derived (n = 74), with a change-point derived for Al at 615 mg kg⁻¹ within a lower and upper confidence interval of 508 and 716 mg kg⁻¹, respectively.

Figure 3. Ratios of Mehlich3-Al to M3-P (Al:P) plotted against (a) FeO-P and (b) Morgan's P in non-calcareous (n = 76) separated out from the full data-set. A broken-line regression fitted to both data-set calculated change-points for FeO-P at 43.2 mg kg⁻¹ within lower and upper confidence interval of 32.3 and 53.9 mg kg⁻¹, respectively. The dotted line represents change-point values of Morgan's P and Al:P on the x and y axes, respectively. Morgan's P change-point was derived at 7.3 mg l⁻¹ within lower and upper confidence interval of 5.9 and 8.7 mg l⁻¹, respectively.

Figure 4. The Relationship between Morgan's P and (a) M3-P for both non-calcareous (n = 76) and calcareous soils (n = 44); and (b) Olsen-P for non-calcareous (n = 47) and calcareous (n = 14) soils, with regression lines and confidence intervals showing diverging relationships in both soil groups with smaller M3-P and Olsen-P values, large Morgan's P values in calcareous soils.

644 **Figure 5.** The relationship between Morgan's P and FeO-P in non-calcareous (n = 76) and
645 calcareous (n = 44) soils with overlapping confidence intervals showing comparable values
646 of FeO-P at similar Morgan's P between both soil groups.

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